

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

15

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification⁴ : A01N 25/34, A61K 7/00 A61L 2/16, D06M 16/00	A1	(11) International Publication Number: WO 89/ 03639 (43) International Publication Date: 5 May 1989 (05.05.89)
(21) International Application Number: PCT/GB88/00841 (22) International Filing Date: 10 October 1988 (10.10.88) (31) Priority Application Number: 8724646 (32) Priority Date: 21 October 1987 (21.10.87) (33) Priority Country: GB (71) Applicant (for all designated States except US): FIBRE TREATMENTS (HOLDING) LIMITED [GB/GB]; Smallshaw Industrial Estate, Accrington Road, Burnley, Lancashire BB11 5SR (GB). (72) Inventor; and (75) Inventor/Applicant (for US only) : FELLOWS, Adrian, Neville [GB/GB]; 1 Slater Bank, Hebden Bridge, North Yorkshire (GB).	(74) Agent: BANNERMAN, David, Gardner; Withers & Rogers, 4 Dyer's Buildings, Holborn, London EC1N 2JT (GB). (81) Designated States: AT (European patent), AU, BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), LU (European patent), NL (European patent), SE (European patent), US. Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(54) Title: INSECT REPELLENT (57) Abstract The invention provides a wipe comprising a flexible substrate, to at least a portion of which has been applied water-insoluble active agent which can be transferred to a surface by wiping and an indicator dye which becomes transferred to the surface along with the active agent, thus giving a visible indication of depletion of the active agent. Particularly the active agent is an insect repellent.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	ML	Mali
AU	Australia	GA	Gabon	MR	Mauritania
BB	Barbados	GB	United Kingdom	MW	Malawi
BE	Belgium	HU	Hungary	NL	Netherlands
BG	Bulgaria	IT	Italy	NO	Norway
BJ	Benin	JP	Japan	RO	Romania
BR	Brazil	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	LI	Liechtenstein	SN	Senegal
CH	Switzerland	LK	Sri Lanka	SU	Soviet Union
CM	Cameroon	LU	Luxembourg	TD	Chad
DE	Germany, Federal Republic of	MC	Monaco	TG	Togo
DK	Denmark	MG	Madagascar	US	United States of America
FI	Finland				

WO 89/03639

PCT/GB88/00841

-|-

Insect Repellent

In previous patent number 2007096 and patent application number 8518736 we have described methods of indicating the presence of impregnants or treatments in substrates of various kinds. Particularly, these inventions have been of value in indicating the continuing presence of useful levels of water soluble disinfectant compositions on wiping cloths for various applications within the food, health-care, dairy and other industries.

The present invention addresses itself to the need to indicate the remaining presence of useful levels of water-insoluble active agents on flexible substrates such as wipes, pads, cloths, sponges, sponge-cloth, mats, clothing, head-bands, mittens, gloves of woven and nonwoven fabrics, other fibrous materials, animal skin products (e.g. leather) and animal furs. Further, the present invention covers such articles comprising a substrate, a water insoluble active agent, and a visual indicator of the continuing presence or conversely of the depletion of said active agent, which may be a chemical substance, mixture or formulation.

Particularly, the present invention covers substrates having applied thereto, as active agent, insect repellent compositions which may usefully be transferred to inanimate surfaces, human hair or skin, or animal skin, hair, or fur. However, the invention is not limited to insect repellent as active agents. Any chemical agent which could usefully be transferred to a surface, to modify the manner in which

SUBSTITUTE SHEET

WO 89/03639

PCT/GB88/00841

-2-

the surface interacts with its environment could be used for instance insecticides, herbicides, fungicides, rodenticides, biocides, timber treatment agents, rot proofing agents, corrosion inhibitors, cosmetics, dermatological agents, polish, pheromone attractants or combinations thereof.

According to one aspect of the invention, we provide a wipe comprising a flexible substrate, to at least a portion of which has been applied a water-insoluble active agent which can be transferred to a surface by wiping and an indicator dye which becomes transferred to the surface along with the active agent, thus giving a visible indication of depletion of the active agent.

Preferably, active agent has been applied to the substrate as a first step, and the indicator dye in a subsequent step. In that case, the indicator dye is preferably applied in conjunction with a substance in which the dye is soluble but in which the active agent is at least partially insoluble. That substance is preferably a wax.

More preferably, the indicator dye and the wax are applied in the form of a solution at a temperature above ambient temperature, the solvent being such that the wax is at least partially insoluble in it at ambient temperature. That solvent is preferably more of the active agent that was already applied in the first step.

Thus, we provide a flexible substrate, such as a cloth, wipe, sponge pad or other form of substrate, preferably a woven or nonwoven textile or fabric to which has been applied, uniformly or otherwise,

SUBSTITUTE SHEET

WO 89/03639

PCT/GB88/00841

-3-

an agent comprising an active substantially water insoluble component which component may be in formulation with other materials and may be in aqueous emulsion or dispersion at its time of application to the substrate. Further, there is applied to this treated substrate an indicator system which comprises one or more components which are at least partially insoluble, and preferably are substantially insoluble, in the active component at normal ambient temperatures: along with the dye or pigment, which may be soluble or insoluble in the active component. The said indicator is capable of application in a discreet and clearly delineated form, such as stripes, patterns, images or logos, and will maintain this distinct format subsequent to production and throughout the proper storage of the product. However, upon usage of the product the indicator will fade, blur, or otherwise start to disappear as it is transferred to the requisite surface along with the active component, e.g. when an insect repellent wipe is rubbed on the skin.

More precisely, flexible substrates used in this invention are preferably woven or nonwoven fabrics composed of natural or synthetic fibres, particularly cellulosic fibres such as viscose, or petrochemical derived polymers such as polyethylene, polypropylene, polyamides, polyesters.

In an insect repellent embodiment of the invention the insect repellent agent is chosen from among those chemicals known to have the relevant properties of safety in use combined with repellent properties. The following are examples benzil, benzyl benzoate, 2,3,4,5-bis(butyl-2-ene)-tetrahydrofurfural, butoxypolypropylene

SUBSTITUTE SHEET

WO 89/03639

PCT/GB88/00841

-4-

glycol, N-butylacetanilide, n-butyl 6,6-dimethyl-5,6-dihydro-1,4-pyrone-2-carboxylate, dibutyl adipate, dibutyl phthalate, di-n-butyl succinate, N,N-diethyl-m-toluamide, dimethyl carbate (cis-dimethyl bicyclo[2.2.1]-5-heptene-2,3-dicarboxylate), dimethyl phthalate, 2-ethyl-2-butyl-1,3-propanediol, 2-ethyl-1,3-hexanediol, di-n-propyl isocinchomeronate, 2-phenylcyclohexanol, n-propyl N,N-diethylsuccinamate or citronellol.

In preferred compositions of this invention the insect repellent agent is N,N-diethyl-m-toluamide either alone or in combination with other insect repellent agents. This material is preferably but not of necessity applied to the substrate in the form of a simple aqueous emulsion. A suitable emulsifier is a linear alcohol mixed ethoxylate propoxylate block copolymer.

The indicator system is preferably prepared in the form of a liquid made by dissolving a wax in a solvent, which solvent may be the active chemical, e.g. diethyl toluamide, or may be some other solvent. The wax may be a natural or synthetic hydrocarbon wax, a wax acid, ester, partially saponified wax, or polyethylene or polypropylene glycol, or a mixture thereof. It is preferred that the wax has a melting point of above 50°C. A small amount of a wax-soluble dye such as Waxoline Blue, Solvent Green 3, Solvent Yellow 12, Solvent Red 19, 23, 24, 27 or 45, Solvent Black 3 is added to the wax and co-solvent. Alternatively an insoluble pigment such as Ultramarine may be utilised. When all three components have dissolved and/or mixed, the indicator composition is applied to the impregnated substrate.

SUBSTITUTE SHEET

WO 89/03639

PCT/GB88/00841

-5-

Two example of insect repellent wipes within the scope of this invention are as follows:

Example 1SUBSTRATE

Viscose polypropylene nonwoven fabric - 50 gram per square metre

IMPREGNANT

N,N-diethyl-m-toluamide (insect repellent agent) dispersed in water with the aid of a nonionic wetting agent, e.g. linear alcohol ethoxylate

N,N-diethyl-m-toluamide	2% - 75%
Emulsifying agent	2% - 25%
Water	33% - 95%

The impregnant is then applied to the fabric to give a loading of between 2.5 and 50% by weight of Diethyl toluamide; but preferably between 10 and 25%.

To this impregnated fabric is added the indicator formulation made up as follows:

N,N-diethyl-m-toluamide	25% - 75%
Wax	25% - 75%

SUBSTITUTE SHEET

WO 89/03639

PCT/GB88/00841

-6-

Dye Trace, to required depth of colour.

An especially preferred indicator dye formulation would be:

N,N-diethyl-m-toluamide	75%
Wax (hydrocarbon)	25%
Waxoline Blue	? Trace

This indicator formulation is applied in stripes or some other format to the impregnated and dried substrate, such that a proportion of the substrate having been impregnated receives the indicator. In an alternative embodiment it is possible to apply the indicator over the whole of the substrate, and in such a case only a very small proportion, of wax or even no wax at all need to be present.

Example 2

SUBSTRATE

Viscose polyester nonwoven

IMPREGNANT

N,N-diethyl-m-toluamide

INDICATOR

Dimethyl phthalate

Polyethylene glycol 6000

Sudan III dye

SUBSTITUTE SHEET

WO 89/03639

PCT/GB88/00841

-7-

If desired other components may be included such as fragrances, emollients, sun screens, etc.

Example 3SUBSTRATE

Viscose polypropylene nonwoven.

IMPREGNANT

N,N Diethyl-M-Toluamide

INDICATOR

N,N Diethyl-M-Toluamide

Hydrocarbon wax

Polyethylene glycol 4000

Ultramarine pigment

This formulation is suitable for direct application of the DEET as neat raw material followed by gravure or flexographic printing of the indicator component. The ratio of components in the indicator system may be varied depending on the particular product characteristics required. A typical formulation would be 3 PARTS DEET to 1 PART equal proportions of the two waxes, with a final pigment concentration of between 5 and 20% by weight of the indicator composition.

SUBSTITUTE SHEET

WO 89/03639

PCT/GB88/00841

-8-

CLAIMS

1. A wipe comprising a flexible substrate, to at least a portion of which has been applied water-insoluble active agent which can be transferred to a surface by wiping and an indicator dye which becomes transferred to the surface along with the active agent, thus giving a visible indication of depletion of the active agent.
2. A wipe according to claim 1, wherein active agent has been applied to the substrate in a first step, and the indicator dye in a subsequent step.
3. A wipe according to claim 2, wherein the indicator dye is applied in conjunction with a solvent for the dye and also a substance with which the dye and solvent are only miscible above normal ambient temperature.
4. A wipe according to claim 3, wherein the said substance is a wax
5. A wipe according to claim 4, wherein the indicator dye and the wax are applied in the form of a solution at a temperature above ambient temperature, the solvent being such that the wax is at least partially insoluble in it at ambient temperature.

SUBSTITUTE SHEET

WO 89/03639

PCT/GB88/00841

-9-

6. A wipe according to claim 5, wherein active agent in addition to that applied in the first step is utilised as the solvent for the wax in the second step.
7. A wipe according to any proceeding claim wherein the active agent is or includes N,N-diethyl-m-toluamide.
8. A wipe according to any of claims 1 to 6 wherein the active ingredient is or includes an insect repellent agent, for example benzil, benzyl benzoate, 2,3,4,5-bis(butyl-2-ene)-tetrahydrofurfural, butoxypolypropylene glycol, N-butylacetanilide, n-butyl 6,6-dimethyl-5,6-dihydro-1,4-pyrone-2-carboxylate, dibutyl adipate, dibutyl phthalate, di-n-butyl succinate, dimethyl carbate (cis-dimethyl bicyclo(2.2.1)-5-heptene-2,3-dicarboxylate), dimethyl phthalate, 2-ethyl-2-butyl-1,3-propanediol, 2-ethyl-1,3-hexanediol di-n propyl isocinchomeronate, 2-phenylcyclohexanol, n-propyl N,N-diethylsuccinamate or citronellol.
9. A wipe according to claim 4, wherein the wax is a natural or synthetic hydrocarbon wax, a waxy acid or ester, partially saponified ester or polyethylene or polypropylene glycol, or a mixture thereof.
10. A wipe according to claim 4 or ~~9~~, wherein the indicator dye is Waxoline Blue, Solvent Green 3, Solvent Yellow 12, Solvent Red 19, 23, 24, 27 or 45, Solvent Black 3.

SUBSTITUTE SHEET

WO 89/03639

PCT/GB88/00841

-10-

A wipe according to claim 4 or 9 wherein the indicator dye is an insoluble pigment.

11. A wipe according to any preceeding claim, wherein the substrate is chosen from a woven or nonwoven fabric comprising natural or synthetic fibres, or petrochemical derived polymers such as polyethylene, polypropylene, polyamides, or polyesters.
12. A wipe according to any preceeding claim, wherein the active agent is chosen from insecticides, herbicides, fungicides, rodenticides, biocides, timber treatment agents, rot proofing agents, corrosion inhibitors, cosmetics, dermatological agents, polish, pheromone attractants or combinations thereof.

SUBSTITUTE SHEET

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 88/00841

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ¹		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ⁴ : A 01 N 25/34; A 61 K 7/00; A 61 L 2/16; D 06 M 16/00		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC ⁴	A 01 N; A 61 K; A 61 L; D 06 M	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	GB, A, 2007096 (EXTERMA GERM PRODUCTS) 16 May 1979 see claims cited in the application --	1-12
A	EP, A, 0210034 (FIBRE TREATMENTS) 28 January 1987 see claims cited in the application --	1-12
A	US, A, 3818533 (F.F. SCHEUER) 25 June 1974 see claims --	3,4,9
A	GB, A, 2180752 (T.K. INDUSTRIAL SUPPLIES) 8 April 1987 see claims 1,4 --	1-12
A	US, A, 4248597 (G.W. MCNEELY) 3 February 1981 see claims 1-3 --	1-12
./.		
<p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
27th January 1989		22.02.89
International Searching Authority		Signature of Authorized Officer
EUROPEAN PATENT OFFICE		P.C.G. VAN DER PUTTEN

International Application No.

PCT/GB 88/00841

-2-

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
------------	--	----------------------

A	Chemical Patents Index, Basic Abstracts Journal, Section C, week 8621, 16 July 1986, Derwent Publications Ltd, (London, GB), & JP, A, 61072701 (MISHIMA SEISHI) 14 April 1986 see abstract no. 135125	1-12
---	---	------

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

GB 8800841

SA 24663

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 08/02/89
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB-A- 2007096	16-05-79	BE-A- 870799	15-01-79
		LU-A- 80279	16-03-79
		NL-A- 7809740	29-03-79
		FR-A, B 2404067	20-04-79
		DE-A, C 2841749	05-04-79
		JP-A- 54055677	02-05-79
		AU-A- 4001478	27-03-80
		CH-A, B 628198	26-02-82
		CA-A- 1131116	07-09-82
		AU-B- 527441	03-03-83
		SE-A- 7810087	28-03-79
		SE-B- 430797	12-12-83
EP-A- 0210034	28-01-87	AU-A- 6041086	29-01-87
		US-A- 4678704	07-07-87
US-A- 3818533	25-06-74	US-A- 3619280	09-11-71
GB-A- 2180752	08-04-87	None	
US-A- 4248597	03-02-81	CA-A- 1105781	28-07-81

EPO FORM P0479

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82